

Dissipative Particle Dynamics with energy conservation

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Dissipative particle dynamics (DPD) does not conserve energy and this precludes its use in the study of thermal processes in complex fluids. We present here a generalization of DPD that incorporates an internal energy and a temperature variable for each particle. The dissipation induced by the dissipative forces between particles is invested in raising the internal energy of the particles. Thermal conduction occurs by means of (inverse) temperature differences. The model can be viewed as a simplified solver of the fluctuating hydrodynamic equations and opens up the possibility of studying thermal processes in complex fluids with a mesoscopic simulation technique.

I. INTRODUCTION

Dissipative particle dynamics constitutes a valuable tool for mesoscopic simulations of complex fluids. It was introduced by Hoogerbrugge and Koelman [1], [2] and has received growing interest in view of its potentiality in the study of complex flow problems as those arising in porous flow [1], colloidal suspensions [2]- [4], polymer suspensions [5], or multicomponent flows [6]. The technique has received a considerable theoretical backup [7]- [11] that provides solid ground for its use.

DPD faces, however, a conceptual problem in that energy is not conserved: the dissipative particles interact with dissipative forces that depend on the relative velocities between particles. For this reason, a DPD system cannot sustain a temperature gradient as it has been pointed out by Marsh et al. [10]. Nevertheless, in the picture where the dissipative particles are understood as droplets or mesoscopic clusters of atoms [1,12] it is apparent that the dissipated energy due to friction must be invested into increasing the internal energy of the cluster. Therefore, we propose in this letter to introduce an additional variable ϵ_i which is interpreted as the internal energy of each particle. Along this new variable we introduce an entropy variable $s_i = s(\epsilon_i)$ and a temperature $T_i = [\partial s_i / \partial \epsilon_i]^{-1}$.

The variation of the internal energy must involve two different processes. On one hand, temperature differences between particles produce variations in the internal energies through “heat conduction”. On the other, the friction forces dissipate energy which is transformed into internal energy through “viscous heating”. Let us analyze each process separately.

II. CONDUCTION

Let us assume for a while that the N dissipative particles of the system are at rest at positions \mathbf{r}_i . We formulate the following equation of motion for the internal energy of each particle

$$\dot{\epsilon}_i = \kappa \sum_j \left(\frac{1}{T_i} - \frac{1}{T_j} \right) \omega(r_{ij}) + \sum_j \tilde{q}_{ij} \quad (1)$$

This is a discrete fluctuating Fourier equation of heat conduction with κ playing the role of a thermal conductivity. We note that the thermodynamic quantity conjugated to the internal energy is the inverse of the temperature rather than the temperature itself. $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between particles i, j and the weight function $\omega(r)$ determines the range of influence between particles. The random process \tilde{q}_{ij} mimics the random heat flux that occurs spontaneously due to thermal fluctuations [13]. This random “heat flux” is assumed to be antisymmetric under particle interchange, this is, $\tilde{q}_{ij} = -\tilde{q}_{ji}$ in such a way that the total internal energy of the system is conserved $\frac{d}{dt} \sum_i \epsilon_i = 0$ if only a heat conduction process occurs.

The Langevin equations (1) have a mathematical well-defined correspondence in the form of a stochastic differential equation (SDE),

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$$d\epsilon_i = \kappa \sum_j \left(\frac{1}{T_i} - \frac{1}{T_j} \right) \omega(r_{ij}) dt + \sum_j \alpha \tilde{\omega}(r_{ij}) dW_{ij}^\epsilon \quad (2)$$

where we have expressed the random “heat flux” \tilde{q}_{ij} from particle i to j in terms of the increments of the Wiener process dW_{ij}^ϵ . The function $\tilde{\omega}(r_{ij})$ provides the range of interaction and α is an overall noise amplitude. The increments of the Wiener process are antisymmetric under particle interchange $dW_{ij}^\epsilon = -dW_{ji}^\epsilon$ and satisfy the mnemotechnical Ito rule

$$dW_{ii'}^\epsilon dW_{jj'}^\epsilon = [\delta_{ij} \delta_{i'j'} - \delta_{ij'} \delta_{i'j}] dt \quad (3)$$

Following a standard procedure [14] it is possible to obtain the Fokker-Planck equation (FPE) that is mathematically identical to the SDE (2). The result is

$$\partial_t \rho_t(\epsilon) = -\kappa \sum_{ij} \omega(r_{ij}) \frac{\partial}{\partial \epsilon_i} \left[\frac{1}{T_i} - \frac{1}{T_j} \right] \rho_t(\epsilon) + \frac{1}{2} \sum_{ij} \alpha^2 \tilde{\omega}^2(r_{ij}) \left[\frac{\partial^2}{\partial \epsilon_i \partial \epsilon_i} - \frac{\partial^2}{\partial \epsilon_i \partial \epsilon_j} \right] \rho_t(\epsilon) \quad (4)$$

where $\rho_t(\epsilon)$ is the density of probability of finding a particular distribution $\epsilon_1, \dots, \epsilon_N$ of internal energies in each particle.

It is noteworthy that if one assumes the detailed balance condition $\alpha^2 = 2\kappa$, and $\omega(r) = \tilde{\omega}^2(r)$, then the FPE becomes

$$\partial_t \rho_t(\epsilon) = L^{HC} \rho_t(\epsilon) \quad (5)$$

where the heat conduction operator is given by

$$L^{HC} = \kappa \sum_{ij} \omega(r_{ij}) \frac{\partial}{\partial \epsilon_i} \left[\frac{1}{T_j} - \frac{1}{T_i} + \left[\frac{\partial}{\partial \epsilon_i} - \frac{\partial}{\partial \epsilon_j} \right] \right] \quad (6)$$

The FPE (5) admits the following unique equilibrium solution

$$\rho_{eq}(\epsilon) = \frac{1}{Z} \exp \left\{ \sum_i s(\epsilon_i) \right\} \mathcal{P}(\sum_k \epsilon_k) \quad (7)$$

where Z is the normalizing factor and $\mathcal{P}(\sum_k \epsilon_k)$ is a function of the total internal energy and will be discussed in the next section. This is the Einstein’s formula for energy fluctuations in the presence of energy conservation. Note that at equilibrium the intensive parameters T_i^{-1} are equal on average [15]

$$\begin{aligned} \left\langle \frac{1}{T_i} \right\rangle &= \int d\epsilon \frac{\partial}{\partial \epsilon_i} [\exp S(\epsilon)] \mathcal{P}(\sum_k \epsilon_k) \\ &= - \int d\epsilon \exp S(\epsilon) \frac{\partial}{\partial \epsilon_i} \mathcal{P}(\sum_k \epsilon_k) = - \int d\epsilon \exp S(\epsilon) \frac{\partial}{\partial \epsilon_j} \mathcal{P}(\sum_k \epsilon_k) = \left\langle \frac{1}{T_j} \right\rangle \end{aligned} \quad (8)$$

On the other hand, if one computes with the method of Lagrange multipliers the most probable distribution $\tilde{\epsilon}_1, \dots, \tilde{\epsilon}_N$ subject to the conservation of internal energy one also obtains $T(\tilde{\epsilon}_i) = T(\tilde{\epsilon}_j)$ [15].

III. VISCOUS HEATING

When the particles have certain velocities \mathbf{v}_i , the DPD model prescribes the following equations of motion [7]

$$\begin{aligned} d\mathbf{r}_i &= \mathbf{v}_i dt \\ d\mathbf{v}_i &= \left[\sum_{j \neq i} \frac{1}{m} \mathbf{F}_{ij}^C(\mathbf{r}_{ij}) - \sum_{j \neq i} \gamma_{ij} B(r_{ij}) (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij} \right] dt + \sum_{j \neq i} \sigma_{ij} \tilde{B}(r_{ij}) \mathbf{e}_{ij} dW_{ij}^v \end{aligned} \quad (9)$$

where \mathbf{F}_{ij}^C is a conservative force that derives from a potential $V(r_{ij})$, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity, and the functions $B(r), \tilde{B}(r)$ provide the range of the forces. In the original DPD algorithm the friction coefficient γ_{ij} and

the noise amplitude σ_{ij} where assumed to be identical for all pairs, this is, $\gamma_{ij} = \gamma$ and $\sigma_{ij} = \sigma$. We need to be more general now due to the temperature variations. The increments of the Wiener process are symmetric under particle interchange, $dW_{ij}^v = dW_{ji}^v$, in order to ensure momentum conservation [7]. They satisfy the Ito mnemotechnical rule

$$dW_{ii'}^v dW_{jj'}^v = [\delta_{ij}\delta_{i'j'} + \delta_{ij'}\delta_{i'j}]dt \quad (10)$$

From the equation of motion (9) it is possible to evaluate an infinitesimal increment of the total mechanical energy defined as $E_{mec} = \frac{1}{2} \sum'_{ij} V(r_{ij}) + \sum_i \frac{1}{2} m v_i^2$. The prime in the summatory excludes the terms $i = j$. Using Ito calculus with the rules (10) we obtain

$$dE_{mec} = -\frac{m}{2} \sum'_{ij} B(r_{ij}) \gamma_{ij} (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2 dt + \frac{m}{2} \sum'_{ij} \tilde{B}^2(r_{ij}) \sigma_{ij}^2 dt + \frac{m}{2} \sum'_{ij} \sigma_{ij} \tilde{B}(r_{ij}) (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij}) dW_{ij}^v \quad (11)$$

We make the assumption that all the dissipated energy (11) is invested in rising the total internal energy $\dot{E} = -\sum_i \dot{\epsilon}_i$ in such a way that the *total* energy $E + \sum_i \epsilon_i$ is exactly conserved. This can be achieved simply by considering the following SDE for the internal energy

$$d\epsilon_i = \frac{m}{2} \left[\sum_j \left[B(r_{ij}) \gamma_{ij} (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2 - \sigma_{ij}^2 \tilde{B}^2(r_{ij}) \right] dt - \sum_j \sigma_{ij} \tilde{B}(r_{ij}) (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij}) dW_{ij}^v \right] \quad (12)$$

Now, if we assume that both processes of conduction and viscous heating are operating then the proposed equations of motion are given by

$$\begin{aligned} d\mathbf{r}_i &= \mathbf{v}_i dt \\ d\mathbf{v}_i &= \left[\sum_{j \neq i} \frac{1}{m} \mathbf{F}_{ij}^C(\mathbf{r}_{ij}) - \sum_{j \neq i} \gamma_{ij} B(r_{ij}) (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij} \right] dt + \sum_{j \neq i} \sigma_{ij} \tilde{B}(r_{ij}) \mathbf{e}_{ij} dW_{ij}^v \\ d\epsilon_i &= \frac{m}{2} \left[\sum_j \left[B(r_{ij}) \gamma_{ij} (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2 - \sigma_{ij}^2 \tilde{B}^2(r_{ij}) \right] dt - \sum_j \sigma_{ij} \tilde{B}(r_{ij}) (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij}) dW_{ij}^v \right] \\ &\quad + \kappa \sum_j \left(\frac{1}{T_i} - \frac{1}{T_j} \right) \omega(r_{ij}) dt + \sum_j \alpha \tilde{\omega}(r_{ij}) dW_{ij}^\epsilon \end{aligned} \quad (13)$$

We postulate that dW_{ij}^v and dW_{ij}^ϵ are uncorrelated.

These stochastic differential equations have associated an equivalent Fokker-Planck equation that governs the evolution of the distribution function ρ_t of the all the variables of the system. By assuming

$$\begin{aligned} \tilde{\omega}^2(r) &= \omega(r) \\ \alpha^2 &= 2\kappa \\ \tilde{B}^2(r) &= B(r) \end{aligned} \quad (14)$$

and after some straightforward although lengthy algebra the following FPE results

$$\partial_t \rho_t = L^{FP} \rho_t = [L^C + L^{VH} + L^{HC}] \rho_t \quad (15)$$

where L^C is the usual Liouville operator of the conservative system

$$L^C \equiv - \left[\sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i,j} \frac{\mathbf{F}_{ij}^C}{m} \frac{\partial}{\partial \mathbf{v}_i} \right] \quad (16)$$

The heat conduction operator L^{HC} is given by (6) and the viscous heating operator L^{VH} is given by

$$L^{VH} = \frac{1}{2} \sum'_{ij} B(r_{ij}) L_{ij} \left[\gamma_{ij} (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij}) + L_{ij} \frac{\sigma_{ij}^2}{2} \right] \quad (17)$$

where the operator L_{ij} is defined by

$$L_{ij} = \mathbf{e}_{ij} \cdot \left[\frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j} - \frac{m}{2} \mathbf{v}_{ij} \left[\frac{\partial}{\partial \epsilon_i} + \frac{\partial}{\partial \epsilon_j} \right] \right] \quad (18)$$

It is most important to realize that the Fokker-Planck operator in (15) satisfies $L^{FP}f(E) = 0$ and $L^{FP}g(\mathbf{P}) = 0$ for any arbitrary functions f, g of the total energy and total momentum. This crucial property is a reflection of the conservation of energy and momentum of the SDE (13).

As in the previous section, the requirement that the FPE has a prescribed equilibrium solution imposes certain constraints on the different functions and parameters of the model. We postulate that the equilibrium distribution function is given by

$$\rho_{eq}(r, v, \epsilon) = \frac{1}{Z} \exp\left\{\sum_i s(\epsilon_i)\right\} P(E_{tot}(r, v, \epsilon), \mathbf{P}) \quad (19)$$

where $P(E, \mathbf{P})$ is a function of the total energy and momentum to be determined below. It is easily shown that if $\sigma_{ij} = \sigma$, a constant for all particles, and

$$\gamma_{ij} = \frac{m}{2} \sigma^2 \frac{1}{2} \left[\frac{1}{T_i} + \frac{1}{T_j} \right] \quad (20)$$

then the equilibrium distribution function (19) is the solution of the FPE (5). This non-trivial result (20) constitutes along with (14) the detailed balance conditions for the model. The result (20) is to be compared with the detailed balance condition of the algorithm without internal energy, $\gamma = m\sigma^2/2T$.

We discuss now the meaning of $P(E, \mathbf{P})$ by considering the time-dependent probability density $\mathcal{P}(E, \mathbf{P})$ that the system has a given value of the dynamical invariants E, \mathbf{P} . It is given by

$$\mathcal{P}(E, \mathbf{P}; t) = \int dz \delta(E - E(z)) \delta(\mathbf{P} - \sum_k m \mathbf{v}_k) \rho_t(z) \quad (21)$$

where z is a shorthand for all the variables of the system and $E(z) = \frac{1}{2} \sum_{ij} V(r_{ij}) + \sum_i \frac{1}{2} m v_i^2 + \sum_i \epsilon_i$. The time derivative of (21) is zero, $\partial_t \mathcal{P} = 0$, as can be seen after using the Fokker-Planck equation for $\partial_t \rho_t(z)$ and an integration by parts. This means that the equations of motion do not modify the distribution of dynamical invariants, which is, therefore, determined by the initial distribution function $\rho_0(z)$. By using the equilibrium distribution function $\rho_{eq}(z)$ in (21) one obtains $P(E, \mathbf{P}) = \mathcal{P}(E, \mathbf{P})$ and the function $P(E, \mathbf{P})$ in (19) is determined by the initial distribution of dynamical invariants. A similar argument can be given in classical mechanics where instead of a Fokker-Planck operator a Liouville operator applies [16]. In general, we will assume that $P(E, \mathbf{P}) = P(E) \delta(\mathbf{P})$ because the center of mass of the total system will be selected at rest at the initial time.

A final comment on the meaning of the temperature is in order. The rate of change of mechanical energy is inferred from equation (11),

$$\langle \dot{E}_{mec} \rangle = -\frac{m}{2} \left\langle \sum_{ij} \gamma_{ij} (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})^2 B_{ij} \right\rangle + \frac{m\sigma^2}{2} \left\langle \sum_{ij} B_{ij} \right\rangle \quad (22)$$

The first contribution is the energy dissipated by friction whereas the second contribution is the energy provided by the noise. At equilibrium both terms are equal and there is no net variation of the mechanical energy, on average. These terms can be computed explicitly with the distribution function (19) by using the invariance of (19) under rotations (see appendix in Ref. [17]). It turns out then that the following relationship is satisfied (for any particle k)

$$\left\langle \frac{\frac{1}{2} m \mathbf{v}_k^2}{\frac{D}{2} T(\epsilon_k)} \sum_{ij} B(r_{ij}) \right\rangle = \left\langle \sum_{ij} B(r_{ij}) \right\rangle \quad (23)$$

where D is the physical dimension of space. This is a precise statement about the relationship between the temperature of the particle and its kinetic energy, at equilibrium. It constitutes the equivalent to the equipartition theorem to which it reduces if all the particles have a constant temperature and consistently the canonical distribution is assumed.

In summary, we have presented an extension of DPD that includes an internal energy variable. The mechanical energy dissipated by friction is transformed into internal energy. In addition, heat conduction occurs. The macroscopic

behavior of the system will be hydrodynamic in the momentum and energy. It is possible to construct a kinetic theory along the lines of Ref. [10] for the DPD model of this letter and obtain balance equations for the momentum and energy. The energy now is a slow independent variable (because it is conserved) and it is possible to have thermal gradients. This opens up the possibility of study a large variety of problems in which thermal processes in complex fluids are of concern.

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